

Claims

1. Continuous process for the production of carbon-based nanotubes, nanofibres  
5 and nanostructures, comprising the following steps:

- generating a plasma with electrical energy,
- introducing a carbon precursor and/or one or more catalysts and/or carrier plasma gas in a reaction zone of an airtight high temperature resistant vessel  
10 optionally having a thermal insulation lining,
- vaporizing the carbon precursor in the reaction zone at a very high temperature, preferably 4000°C and higher,
- guiding the carrier plasma gas, the carbon precursor vaporized and the catalyst through a nozzle, whose diameter is narrowing in the direction of the  
15 plasma gas flow,
- guiding the carrier plasma gas, the carbon precursor vaporized and the catalyst into a quenching zone for nucleation, growing and quenching operating with flow conditions generated by aerodynamic and electromagnetic forces, so that no significant recirculation of feedstocks or products from the quenching  
20 zone into the reaction zone occurs,
- controlling the gas temperature in the quenching zone between about 4000°C in the upper part of this zone and about 50°C in the lower part of this zone and controlling the quenching velocity between  $10^3$  K/s and  $10^6$  K/s
- quenching and extracting carbon-based nanotubes, nanofibres and other nanostructures from the quenching zone,  
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- separating carbon-based nanotubes, nanofibres and nanostructures from other reaction products.

30 2. Process according to claim 1, wherein plasma is generated by directing plasma gas through an electric arc, preferably a compound arc, created by at least two electrodes.

3. Process according to claim 1 or 2, characterized by one or more of the following features:

- 5        a. The plasma is generated by electrodes consisting of graphite;
- b. The arc is created by connecting an AC power source to electrodes, preferably one where the current frequency lies between 50 Hz and 10 kHz;
- c. The absolute pressure in the reactor lies between 0.1 bar and 30 bar;
- d. The nozzle used consists of graphite at its inner surface;
- 10      e. The nozzle is formed as a continuous or stepped cone;
- f. The nozzle used has a downstream end which abruptly expands from the nozzle throat;
- g. The carbon precursor used is a solid carbon material, comprising one or more of the following materials: Carbon black, acetylene black, thermal black, graphite, coke, plasma carbon nanostructures, pyrolytic carbon, carbon aerogel, activated carbon, or any other solid carbon material;
- 15      h. The carbon precursor used is a hydrocarbon preferably consisting of one or more of the following: methane, ethane, ethylene, acetylene, propane, propylene, heavy oil, waste oil, pyrolysis fuel oil, preferably a liquid carbon material;
- 20      i: Solid catalyst is used consisting of one or more of the following materials: Ni, Co, Y, La, Gd, B, Fe, Cu, is introduced in the reaction zone;
- j. A liquid catalyst is used consisting of one or more of the following materials Ni, Co, Y, La, Gd, B, Fe, Cu in a liquid suspension or as organometallic compound, which is preferably added to the carbon precursor and/or to the carrier gas,
- 25      k. A gas carrying a carbon precursor and/or carrying catalyst and/or to produce the plasma and/or to quench the products and/or to extract the products comprises or consists of one or more of the following gases: Hydrogen, nitrogen, argon, carbon monoxide, helium or any other pure gas without carbon affinity and which is preferably oxygen free;

1. The gas temperature in the reaction zone is higher than 4000°C;
- m. The gas temperature in the quenching zone is controlled between 4000°C in the upper part of this zone and 50°C in the lower part of this zone;
- n. The carrier plasma gas flow rate is adjusted, depending on the nature of the carrier plasma gas and the electrical power, between 0.001 Nm<sup>3</sup>/h to 0.3 Nm<sup>3</sup>/h per kW of electric power used in the plasma arc;
- 5 o. The quenching gas flow rate is adjusted, depending on the nature of the quenching gas, between 1 Nm<sup>3</sup>/h and 10 000 Nm<sup>3</sup>/h;
- p. A portion of the off-gas from the reaction is recycled as at least a portion 10 of the gas for generating the plasma,
- q. A portion of the off-gas from the reaction is recycled as at least a portion of the gas for generating the quenching gas,
- r. A carbon precursor is injected through at least one injector, preferably through two to five injectors,
- 15 s. A carbon precursor is injected into the reaction zone,
- t. A carbon precursor is injected with a tangential and/or with a radial and/or with an axial flow component into the reaction zone,
- u. The process is carried out in the total absence of oxygen or in the presence 20 of a small quantity of oxygen, preferably at an atomic ratio oxygen/carbon of less than 1/1000,
- v. If the plasma gas is carbon monoxide, the process is carried out in the presence of oxygen with a maximum atomic ratio oxygen/carbon of less than 1001/1000 in the plasma gas,
- w. One or more of the following products is recovered:

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- i. Carbon black
- ii. Fullerenes
- iii. Single wall nanotubes
- iv. Multi-wall nanotubes
- 30 v. Carbon fibres
- vi. Carbon nanostructures

## vii. Catalyst

4. Reactor to carry out the process of one of the claims directed to processes comprising in open flow communication

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- a. A head section comprising:
  - i. At least two, preferably three electrodes
  - ii. A carbon precursor supply and/or a catalyst supply and/or a gas supply

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for creating an electric arc between the electrodes when a sufficient electric power is supplied, and creating an arc zone, into which the gas from the gas supply can be fed to generate a plasma gas and for heating the carbon precursor at a vaporization temperature higher than 4000°C

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- b. At least one injector for carbon precursor and/or catalyst injection into the reaction zone
- c. A reaction zone where the gas temperature during operation is 4000°C or higher
- d. A quenching zone where the gas temperature is controllable between 4000°C in the upper part of this zone and 50°C in the lower part of this zone
- e. A nozzle shaped choke, narrowing the open flow communication between the reaction zone and the quenching zone.

25 5. Reactor according to claim 4, having substantially interior cylindrical shape.

6. Reactor according to claim 4 or 5, whereby the high temperature exposed surfaces are of graphite containing high temperature resistant material.

30 7. Reactor according to claim 4, 5 or 6 comprising a chamber with a height between 0.5 and 5 m and a diameter between 5 and 150 cm.

8. Reactor in accordance with one of the claims directed to reactors comprising temperature control means for the quenching zone selected from thermal insulating lining, fluid flow, preferably water flow, indirect heat exchange means and flow and/or temperature controlled quench gas injection means.
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9. Reactor in accordance with one of the claims directed to reactors wherein the nozzle shaped choke is a tapering choke followed by an abruptly expanding section.
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10. Reactor in accordance with one of the claims directed to reactors, characterized by one or more apparatus features of one or more of the process claims.
11. Carbon nanostructures having the structure of a linear chain of connected, substantially identical sections of beads, namely spheres or bulb-like units or trumpet shaped units, preferably having a diameter of the spheres of the spherical section of the bulb-like units or respectively the large diameter of the trumpet shaped section in the range of 100 to 200 nanometres, more preferably having all spheres or bulb-units exhibiting nearly the same diameter, and in particular comprising periodic graphitic nano-fibers being characterized by a repetition of multi-wall carbon spheres ('necklace'-like structure), connected along one direction, and several of the spheres containing a metal particle encapsulated in their structure.
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12. Carbon nanostructures in accordance with claim 11, wherein at least 5 beads are connected to one chain, preferably 20 to 50 beads are in one chain.
13. Carbon nanostructures in accordance with one of the claims directed to carbon nanostructures, wherein one or more of the beads is filled with catalyst, in particular with ferromagnetic metal catalyst, more specifically with nickel or nickel/cobalt.
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14. Carbon nanostructures in accordance with one of the claims directed to carbon nanostructures wherein the bulb-like or bell-like are connected to each other by external graphitic cylindrical layers.

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15. Carbon nanotube exhibiting a multi-wall structure, wherein several nanoconical structures (bamboo shaped structures) are stacked, said nanotubular structures preferably possessing a closed end conical tip apex the other end being either open or filled with a metal nanoparticle .

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16. Carbon nanotube in accordance with claim 15 having an external diameter of about 100 to 120 nm and comprising a set of discontinuous conical cavities.

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17. Carbon nanostructures and carbon nanotubes in accordance with one of the claims directed to such products being arranged in a random form, the SEM of which resembles cooked spaghetti.

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18. Carbon nanostructures being single walled and having preferably one or more of the following properties

- one, preferably both ends are open .
- one layer having a diameter between about 0.8 and about 2 nm.
- length of the tubes is a few microns.

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19. Carbon nanostructure having substantially a shape defined by its SEM or TEM view as shown in one of the Figures showing nanostructures.

20. A composite of carbon nanostructures in accordance with one of the claims directed to such carbon nanostructures and a polymer matrix.

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21. A composite according to claim 20 comprising, preferably consisting of, polyethylene, polypropylene, polyamide, polycarbonate, polyphenylenesulfide, polyester.